Theories and Models

This chapter presents various theoretical models relevant to the present experimental investigation. This encompasses thermodynamics of mixing of polymers, free volume theory, theory of hydrodynamic interactions, theory of positron and positronium annihilation in polymers and blends.

2.1 Thermodynamics of Polymer Mixing

Performance of polymer blends depends on the properties of constituent polymers and their arrangement in space. The spatial arrangement is controlled by thermodynamics and flow imposed morphology. Determination of thermodynamic properties such as phase diagram or Flory-Huggins interaction parameter, $\chi_{12}$, is difficult due to the high viscosity of macromolecular species, thus slow diffusion towards equilibrium [1].

Thermodynamics of polymer blends is based on the classical theories of polymer solutions developed by Flory [2], Huggins [3], Prigogine [4], Patterson [5], Sanchez [6] and as well on theories of phase equilibrium and phase separation in solids developed by Cahn [7], Prigogine [4].

The study of thermodynamics of mixing is to determine the conditions of mixing and ranges of mutual solubility of different polymers depending on their chemical nature and molecular mass. According to the general principle of thermodynamics, formation of thermodynamically stable system is accompanied by a decrease in Gibb’s free energy of mixing, $\Delta G$ [1,8,9]:

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} 2.1
One of the two necessary conditions for system stability is that $\Delta G < 0$, which is satisfied if $\Delta H < 0$ and $\Delta S > 0$ or if $\Delta H > 0$ but $|T\Delta S| > |\Delta H|$. If there is a possibility to determine $\Delta G$ for all possible mixture compositions and temperature corresponding to one phase, stable system conditions can be evaluated. However, experimental determination of $\Delta G$ for polymer blends is very complicated because many methods used for this purpose in polymer – solvent system are not applicable to polymer blends. It was proposed that [10] during mixing of two polymers of high molecular weight, the change in enthalpy is responsible for the mixing, considering that contribution of entropy of mixing for $\Delta G$ is extremely small. According to this, it was considered that a system is miscible if $\Delta H < 0$ and immiscible if $\Delta H > 0$. As a rule for polymer solutions in low molecular weight liquids the condition $\Delta H < 0$ corresponds to the condition of miscibility. However, for polymer blends, Slominsky [11,12] showed that this condition is not true and the contribution of entropy cannot be neglected. Calculations of Flory [2] have shown that, by mixing, entropy diminishes, that is $\Delta S < 0$. The contribution of entropy of mixing for the mutual solubility was for the first time evaluated experimentally by Tager [13, 14]. It was found that entropy of mixing of two polymers is not equal to zero but may be either positive or negative. However, for miscible polymers $\Delta S$ was observed to be less than zero [15].

Scott [16] and Tompa [17] proposed the theory of mixing of two polymers for the first time based on Flory-Huggins theory. They used Flory-Huggins equation for Gibb’s free energy of mixing:

$$\Delta G = \left(\frac{RT}{V_s}\right) \left[\frac{\varphi_A}{r_A} \ln \varphi_A + \frac{\varphi_B}{r_B} \ln \varphi_B + \chi_{AB} \varphi_A \varphi_B\right]$$

2.2
where \( V_s \) represents the volume of segment taken equal to the volume of the repeating unit of the polymer chain, \( r_A \) and \( r_B \) are the number of segments of polymer A and B, \( r_i = V_i/V \) (\( V_i \) is the molar volume of component \( i \)), \( \phi_A \) and \( \phi_B \) are volume fractions of components A and B. \( \chi_{AB} \) is a thermodynamic interaction parameter related to the enthalpy of interaction between the different segments of volume \( V_s \). The mixture is at a critical point when,

\[
\frac{\partial^2 \Delta G}{\Delta \phi_A^2} = \frac{\partial^2 \Delta G}{\Delta \phi_A^3} = 0
\]

Critical Values of concentration and interaction parameters are equal, correspondingly, to

\[
(\phi_A)_{crit} = \frac{1}{1 + \sqrt{r_A + r_B}}
\]

\[
(\chi_{AB})_{crit} = \frac{1}{2} \left( \frac{1}{\sqrt{r_A}} + \frac{1}{\sqrt{r_B}} \right)^2
\]

It follows from equation (2.5) that the value \((\chi_{AB})_{crit}\) for high molecular weight (M) polymers mixing should be very small (near zero) and polymers are immiscible at even very small positive heat of mixing.

\( \chi_{AB} \) can be calculated from the relation,

\[
\chi_{AB} = \frac{V_s}{RT} (\delta_A - \delta_B)^2
\]
where $\delta_A$ and $\delta_B$ are solubility parameters of constituent polymers. From this equation it can be realized that the calculated parameter is always positive, since value $(\chi_{AB})_{\text{crit}}$ is close to 0 and contribution of combinatorial entropy (first two terms of equation (2.2)) is negligibly small. Scott’s approach (equation 2.2 and equation 2.6) predict that it is almost impossible to find a miscible polymer pair. Only when $\delta_A$ and $\delta_B$ are almost equal, the calculated value of $\chi_{AB}$ may be below the critical value. On this basis, it was proposed that, to predict miscibility of two polymers in solid state [18,19], the system is miscible only if $\chi_{AB} < (\chi_{AB})_{\text{crit}}$, which possibly happens at equal composition ratio.

Gee in the year 1942 [20] proposed a relation for the heat of mixing of rubber by swelling,

$$\Delta H = V_0 (\delta_o - \delta_2) (1 - \varphi_o)^2$$

where $V_o$ and $\delta$ are molar volume and solubility parameters of liquid and rubber phases and $(1-\varphi_o)$ is the volume fraction of the swollen rubber.

Based on the above relation, Schneier [21] proposed a relation for heat of mixing of polymers in solid state as,

$$\Delta H = W_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left[ \frac{W_2 M_2 \rho_2}{(1-W_2)} - (1-W_1) M_1 \rho_1 \right]$$

where $M_i$ and $\rho_i$ denotes monomer molecular weight and polymer density respectively. It was established that for miscible polymers, values of $\Delta H$ are in the range $10^{-3}$ to $10^{-2}$ J.
The main characteristic of polymer blends is the thermodynamic compatibility or incompatibility which is governed by the phase behaviour of the system. It is necessary to emphasize here that compatibility depends on many factors, principally on temperature and composition. There are almost no fully compatible or incompatible blends, but there are different conditions under which a polymer pair is miscible or immiscible. However, depending on the chemical structure of blend constituents, the window of miscibility may be broad or narrow with respect to temperature and composition [9].

\( \Delta G < 0 \) is necessary, although not a sufficient condition for the stability of the system. Thermodynamic stability for one phase system exists when [1,8,9,22,23],

\[
\begin{align*}
(\text{i}) \quad & \Delta G < 0 \quad \text{and} \quad \left( \frac{\partial^2 \Delta G}{\partial \phi_i^2} \right) > 0 \\
\end{align*}
\]

The variation of \( \Delta G \) as a function of volume fraction of the second polymer is shown in figure 2.1 from which it is clear that three forms of blends ( as mentioned in the introduction chapter) are possible in binary systems. The curves A, B and C represent ‘Immiscible’, ‘miscible’ and ‘Partially miscible’ blend systems respectively [24].

Dependence of miscibility on temperature and composition could be better understood from the phase diagrams, where \( \Delta G \) is shown as function of composition and temperature. *Figures 2.1a and 2.2a* show the behavior of free energy of mixing as a function of the relative composition of a binary mixture at different temperatures. *Figure 2.1b* represents the coexistence curve for a binary mixture with an upper miscibility gap. Figure 2.2b shows the coexistence curve for a binary mixture with a lower miscibility gap [24]. From *figure 2.1a* depicts the behaviour of Gibb’s free energy of mixing (\( \Delta G \)).
For the curve corresponding to $T_4$, (Figure 2.1a) the above said both conditions (Equation 2.9) are satisfied and therefore the system is miscible throughout the composition. For curves corresponding to the temperatures $T_1$, $T_2$ and $T_3$, $\Delta G$ is negative throughout the compositions and hence the first condition is satisfied. However, between the spinodal points the second condition is not satisfied, and therefore the system exhibits immiscibility in this concentration range and exhibits miscibility only at lower and higher concentrations of polymer 2 forming a partially miscible blend. These examples emphasize that phase separation can occur both due to increase in temperature (Figure 2.1b) or decrease in temperature (Figure 2.2b). The temperature below which single phase results is called lower critical solution temperature (LCST) and the temperature above which the single phase results is called upper critical solution temperature (UCST) and the area under the curves in such diagrams where phase separation occurs is called the upper or the lower miscibility gap [24,25].

Figure 2.1: (a) Free energy of mixing as a function of the relative composition of a binary mixture ($T_4 > T_3 > T_2 > T_1$). (b) Phase diagram for binary blends showing LCST behavior.
For any given temperature the two points on the boundary curve for single-phase behaviour can be extrapolated to the horizontal axis to give the composition of the two mixed phases, resulting in phase separation. The curves joining minima or points of inflection are called the binodal and spinodal respectively.

![Diagram](image)

Figure 2.2: (a) Free energy of mixing as a function of the relative composition of a binary mixture \((T_1 > T_2 > T_0 > T_4)\). (b) Phase diagram for binary blends showing UCST behavior.

The binodal separates the stable (single phase) phase from the metastable state, while the spinodal marks the transition from the unstable to metastable region. The area between binodal and spinodal represents the system in metastable state [24]. Therefore, these phase diagrams help in understanding the composition dependent miscibility behavior of polymer blends.

### 2.2 Free volume theory

There are two ways in which the volume occupied by a system can influence Gibb’s free energy of the system. One of these involves the average distance of separation between the molecules and therefore influences ‘G’ through the
energetics of the molecular interactions. The second effect of volume on ‘G’ arises from the contribution of free volume. The number and size of the holes influence ‘G’ through entropy considerations. Each of these volume effects vary differently with changing temperature and each behaves differently on opposite sides of \( T_g \) i.e before and after \( T_g \)[26].

On the basis of these considerations, observed volume of a sample can be written as the sum of volume occupied by the molecules \( (V_o) \) and the free volume \( (V_f) \). Acknowledging that each of these is a function of temperature, we write [26],

\[
V(T) = V_o(T) + V_f(T) \quad 2.10
\]

Using the basic assumption that fluidity in a liquid is due to the presence of free volume, Batchiniski [27,28] proposed a simple relation for free volume and viscosity, which is given by

\[
\eta \propto \frac{1}{V_f} = (V - V_o)^{-1} \quad \text{i.e. } V_f = (V - V_o) \quad 2.11
\]

In this equation, \( \eta \) is the viscosity, \( V_f \) is the free volume, \( V \) is the total volume of the system and \( V_o \) is the volume occupied by the molecules of the system. Equation 2.11 describes the temperature dependence of viscosity qualitatively but correctly and therefore has a profound physical significance, for many systems, especially for polymers in the fluid state. However, this formula appears to be nothing more than a crude approximation.

Later in the year 1952, Doolittle proposed his theory of free volume [29]. This gained great significance in studies on the microstructure of polymers and recently in polymer blends. Determination of free volume holes in terms of size
and its concentration helps in studying the polymer microstructure in a better way. The macroscopic properties, which are derived using free volume approach, are fruitful with the assistance of quantum and statistical mechanical calculations. As such, over the last few decades there has been a great deal of developments in the free volume theory. Doolittle studied the viscosity of n – alkenes experimentally and proposed a relation between free volume and viscosity as

$$\eta = A \exp \left( \frac{B(V - V_f)}{V_t} \right)$$

where $A$ and $B$ are empirical constants.

Doolittle showed that, this expression describes the viscosity of low molecular weight compounds better than Arrhenius equation,

$$\eta = A \exp \left( \frac{-E^*}{RT} \right)$$

where $E^*$ is the activation energy, $R$ is the universal gas constant and $T$ is temperature.

Although these equations relate $\eta$ to different variables, both Doolittle and Arrhenius equations have the same functional form. Just as the activation energy ($E^*$) measures the height of the energy barrier relative to the thermal energy, so $(V - V_t)$ or $V_o$ is measured relative to $V_t$. If $V_t$ and $V_o$ are expressed per molecule, the exponent in the Doolittle equation measures the volume of a molecule ($V_o$ per molecule) relative to the volume of the hole ($V_t$ per hole). When the molecule is large compared to the vacancy it must move into, the viscosity is high; when the molecule is small compared to hole, the viscosity is low. This is the physical significance of Doolittle equation, although one should remember that it is basically of empirical origin but provides physical interpretation of great significance [26].
If ‘Fv’ is considered to be the fraction of volume contributed by the free volume \((V_f/V)\), then equation 2.12 can be rewritten as,

\[
\eta = A \exp \left[ B \left( \frac{1}{F_v} - 1 \right) \right] \tag{2.14}
\]

Now, the constant \(A\) can be eliminated from the above equation by assuming the ratio of two values of \(\eta\) with different values of ‘Fv’.

\[
\frac{\eta_1}{\eta_2} = \exp \left[ B \left( \frac{1}{F_{v1}} - 1 \right) - \left( \frac{1}{F_{v2}} - 1 \right) \right] = \exp \left[ B \left( \frac{1}{F_{v1}} - \frac{1}{F_{v2}} \right) \right]
\]

\[
\ln \left( \frac{\eta_1}{\eta_2} \right) = B \left( \frac{1}{F_{v1}} - \frac{1}{F_{v2}} \right) \tag{2.15}
\]

Consider subscript 2 corresponding to glass transition values and 1 for the values above the glass transition temperature, that is \(T = T_g\), \(F_{v2} = F_{vg}\) and \(F_{v1} = F_{vg} + \alpha_f(T - T_g)\). Then the above equation takes the form,

\[
\ln \left( \frac{\eta(T > T_g)}{\eta(T_g)} \right) = B \left( \frac{1}{F_{vg} + \alpha_f(T - T_g)} - \frac{1}{F_{vg}} \right) = \frac{-(B/F_{vg})(T - T_g)}{(F_{vg}/\alpha_f) + (T - T_g)} \tag{2.16}
\]

where subscript ‘g’ indicates glass transition. \(\alpha_f\) is the temperature coefficient of free volume.

The above equation is the well known WLF equation \([30]\) and it can also be represented as,

\[
\log a_T = \frac{-17.44 (T - T_g)}{51.6 + T - T_g} = \frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \tag{2.17}
\]
here \( \alpha \) is the ratio of the viscosity at temperature \( T \) relative to that at glass transition temperature \( (T_g) \) and is called the shift factor numerical constants \( C_1 \& C_2 \) can be determined by fitting literature data on the viscosity-temperature behaviour of many glass forming substances. The WLF equation (2.17) is generally assumed to be valid for temperatures from \( T_g \) to \((T_g + 100 \, ^{o}C)\) and it is assumed that at \( T < T_g \), the free volume remains unchanged and will be equal to the free volume at \( T_g \). The free volume at \( T_g \) is 2.5% of total polymer volume, which is taken as a universal constant for all polymers \([31,32]\). The temperature dependence of the fractional free volume, ‘\( F_v \)’ at constant pressure and above \( T_g \) is expressed as,

\[
F_v = F_{vg} + \alpha_o (T - T_g)
\]

\[
= 0.025 + \alpha_o (T - T_g)
\]

where \( T \) is in \(^{o}C\), \( F_{vg} \) is the free volume fraction at \( T = T_g \) and its value is 0.025 \([31,32]\), and \( \alpha_o \) is the coefficient of thermal expansion of free volume.

### 2.3 Free volume and Positronium Lifetime

Literature reveals that various theoretical models have been developed in order to explain the visco-elastic properties of polymers based on free volume concept. Theoretical models particularly those developed by positron physicists to connect the free volume holes to the positron lifetime parameters are outlined here. These models are explained in the following paragraphs.

A theoretical study was made by Ferrell \([33]\) using liquid helium as a simple example to understand the pick-off behavior of the Positronium (Ps) in molecular substances. He pointed out that there are two different types of forces acting on the Ps atom, which tend to compensate one another. In this work, it
becomes clear that besides the attractive Vander Waals type dispersion force; there is a repulsive exchange force. In general, the exchange force works against the pick-off force and is probably the dominant reason for the long lifetime in most materials in which Ps is formed. Around 1960, it was realized that the temperature dependence of o-Ps lifetime in molecular media should be associated with density changes in the materials. Quantitatively, more free volume between the molecules results due to a decrease in density. This leads to a smaller overlap between the Ps wave function and the surrounding molecular electrons with which Ps annihilates. Thus, the rate at which the o-Ps pick-off annihilation occurs is inversely proportional to the size of the free volume holes.

A simplified theory was put forth by Brandt, Berko and Walker [34], in which the positron wave function in the field of the electron, to which it is bound, is replaced by the wave function of the Ps atom. Then, the Ps wave function is calculated for different lattice structures in the Wigner - Seitz approximation. This approximation is generally referred to as “free volume model” since the free volume is used as one of the parameters in their calculation. This model relates the o-Ps lifetime to the average free volume size of the material and it is construed that the o-Ps lifetime measures the lattice - Ps interaction. Tabata et al. [35], Ogata and Tao [36] have adopted similar approaches, but the difference is that they considered a unit cell, whose center is the center of Ps atom instead of the center of the molecule of the surrounding substance as used by Brandt et al. [34]. Story [37] suggested a correlation between the lifetimes of o-Ps in a number of plastic materials with their dielectric constants. Khan [38] suggested a correlation between the lifetimes of o-Ps in a number of polymers with their molecular cohesive energy density. The most successful attempt was made by Gray et.al, [39] in which they found that the
quenching cross section of the o-Ps in n-alkenes correlates directly with the electron polarizability of the molecule.

The dependence of pressure on lifetime values were explained by Wilson et al. [40], and they have given a slightly different description that Ps localizes in low-density regions only. The original free volume model developed by Brandt et al. [34] has been refined by the same group by considering the effect of molecular vibrations and including the Ore gap model of Ps yield. In their later work [41] they used the concept that Ps is formed only if a free volume larger than certain critical value exists. According to Thosar et al. [42], the formation and decay of Ps atoms is confined to the free volume ($V_f$) of the molecular material and there is no electron exchange between molecules. Free volume ($V_f$) is considered to be divided into a number of sites of average free volume $V$ occupied by Ps atoms, which are quenched due to pick-off annihilation. The o-Ps lifetime is related to $V$ and the o-Ps intensity, which depends upon the number of sites available for their formation is related to ($V_f/V$). Thus, they obtain a theoretical relationship between the o-Ps lifetime and its intensity to the free volume in molecular materials.

Let us discuss now the model that is used in this work to evaluate the average size of free volume holes. This model connects o-Ps lifetime to free volume radius. We start from the positron lifetime ($\tau$), which is the reciprocal of the integral of the positron density ($\rho_+$) and the electron density ($\rho_-$) at the site of annihilation [43], which is written as

$$\tau = \text{const} \left( \int \rho_+ \rho_- \, dr \right)^{-1} \quad 2.19$$

The constant in the equation 2.19 is due to normalization and is related to the number of electrons involved in annihilation. To know the values of
experimental positron parameter $\tau$, one must relate the electron densities with the molecular size. The exact solution of $\rho_+^{\pm}$ and $\rho_-$ are intractable quantum mechanical problem. As of now, only approximated approach is feasible. One approach is based on two strategies: (1) to obtain the best $\rho_+$ without wasting much effort in solving for $\rho_-$ or $\tau$. (2) to obtain a theoretical equation by incorporating the existing experimental positron data, which are plenty at the moment, and to correlate these data with the parameters of free volume holes using a semi-empirical equation. Further, Tao's model [44] for the molecular liquids, suggests that the Ps atom be highly localized in a cavity created by the balance of various molecular forces inside the liquid. This localized Ps lifetime, in particular the o-Ps lifetime is found to have a relation with the free volume size.

Following the ideas from Tao's model [44], a simple relation was developed by Nakanishi et al. [45,46] between o-Ps lifetime and the free volume radius for the case of polymers in solid phase. Accordingly, Ps atom is considered to be localized in a spherical box (free volume), which is schematically shown in Figure 2.3. The radial part of the Schrödinger equation for the center of mass motion of Ps is given by

$$\left\{-\frac{\hbar}{2m}\left[\left(\frac{d^2}{dr^2}\right) - \frac{l(l+1)}{r^2}\right] + V(r) - E_n\right\}\psi_{Ps} = 0$$

where

- $V(r) = 0$ at $r > R_o$
- $V(r) = \infty$ elsewhere.

The solution for the above equation can be written as

$$\psi_{Ps} = \frac{1}{2\pi R_o}\left(\sin\left(\frac{\pi r}{R_o}\right)\right) \quad 0 \leq r \leq R_o$$

$$= 0 \quad \text{elsewhere}$$
The energy eigen value for Ps atom in the $n^{th}$ state becomes

$$E_n = \left( \frac{n^2 \hbar^2 \pi^2}{2mR_0^2} \right)$$

The annihilation rate calculation requires the electron density ($\rho$). For this, Nakanishi et. al [45,46] have used a semi-empirical approach after Tao [44] and Eldrup et.al [47] which assumes a homogeneous electron layer with a thickness $\Delta R = R_o - R$ inside the potential well. The probability of Ps in the ground state inside this electron layer is then given by

$$P = 4\pi \int_{R}^{\infty} \left| \Psi(r) \right|^2 r^2 dr$$

$$= 1 - \left( \frac{R}{R_0} \right) + \left( \frac{1}{2\pi} \right) \sin \left( \frac{2\pi R}{R_0} \right)$$

Assuming the annihilation rate of o-Ps inside the electron layer equal to 2 ns$^{-1}$, which is the spin averaged annihilation rate of p-Ps and o-Ps [48], the o-Ps annihilation rate as a function of free volume radius $R$ is given by [49]

$$\lambda = \frac{1}{\tau_3} = 2P$$

$$= 2 \left[ 1 - \left( \frac{R}{R_0} \right) + \left( \frac{1}{2\pi} \right) \sin \left( \frac{2\pi R}{R_0} \right) \right] \text{ns}^{-1}$$

In the above equation $R_o = R + \Delta R$, where $\Delta R$ is the thickness of the electron layer which is treated as an empirical or fitting parameter. Figure 2.3 displays this thickness as the overlap between the wave functions of the electron and the positronium. Nakanishi et. al [45,46] determined $\Delta R$, by fitting equation 2.23 with the measured $\tau_3$ values and the known hole sizes in molecular substances.
such as zeolites [49,50]. The best-fitted value of $\Delta R$ for all known data is found to be 1.656 Å. This equation is adequate in the determination of the average free volume hole size if o-Ps lifetime is measured. The same group [49] have tried to further improve the result by including a finite potential depth instead of an infinite one and the results obtained were found to be similar to the one described above. The radius of the free volume hole $R$ so obtained can be used to evaluate the average free volume hole size as

$$V_f = \frac{4\pi R^3}{3}$$

2.24

From this value of average free volume size, the fractional free volume $F_v$ of the given polymer is then calculated as [45]

$$F_v = C \left( \frac{4\pi R^3}{3} \right) I_3 (\%)$$

2.25

Here, $I_3$ is the o-Ps intensity and $C$ is the structural constant which can be obtained from a measurement of the thermal expansion coefficient of free volume.
On the basis of free volume model, Kelly and Bueche in year 1961 derived the composition dependent free volume additivity of the blend components for the binary mixtures [51].

According to this theory, at constant pressure and temperature, the fractional free volume $F_v$ of the blend is given by

$$ F_v = w_1 F_{v1} + w_2 F_{v2} $$  \hspace{2cm} (2.26)

where $w_1$, $w_2$, $F_{v1}$ and $F_{v2}$ are the weight fractions and fractional free volumes of component 1 and 2 respectively in the blend.

As discussed in Chapter 1, the formation of miscible blend depends on the exothermic heat of mixing, which usually stems from the strong intermolecular forces. Therefore, in case of miscible polymer blends, a reduction in free volume occurs corresponding to a negative change in volume due to favourable interactions between blend components. This reduction results in the negative deviation of the fractional free volume from equation (2.26) for a wide range of composition and it is most commonly reported for miscible blends in literature [52, 53-60]. Furthermore, it has been suggested that for miscible blends, the decrease in free volume due to blending is related to interaction between dissimilar chains, segmental conformations and packing of component polymers results wherever Van der Waals type interactions are involved [52,53-60,61-63]. For a binary mixture based on the work of Wu [64], a relation has been proposed by Jean et.al, in which they introduced an interaction parameter $\beta$ to represent the interaction between dissimilar chains and is given as,

$$ F_v = F_{v1} \phi_1 + F_{v2} \phi_2 + \beta F_{v1} F_{v2} \phi_1 \phi_2 $$  \hspace{2cm} (2.27)

where $F_{v1}$ & $F_{v2}$ are the fractional free volumes and $\phi_1$ & $\phi_2$ are the volume fractions of component 1 and 2 respectively. It has been reported that, for a
miscible polymer blend interchain interaction parameter $\beta$ shows negative values for the entire range of compositions studied [52,53-60], and for an immiscible blend it shows positive values [52,56,57,58,64,65]. In the present work, these additivity relations will be used in chapter 4 and 5 to understand the free volume behavior of blends and to decide whether the blend is miscible or immiscible and also to explore how good this parameter is for the said purpose. In the introduction chapter section 1.7.6, we discussed the limitation of the free volume parameters in studying the interfacial modifications brought in to blend system and accordingly we developed a new method measuring the miscibility properties in polymer blends by exploiting the usefulness of hydrodynamic interaction between blend constituents particularly at the interface [58]. In the following section, we will briefly discuss the theory of hydrodynamic interaction.

2.4 Theory of Hydrodynamic Interactions

As briefly in the introduction chapter, we have made use of the concept of hydrodynamic interactions from the free volume approach to understand the interfacial properties in polymer blends. To understand the behavior of polymer in dilute or concentrated solutions, or in molten form, a number of models have been proposed. These models include the scrutiny of the behavior of mechanical models in the simplest mechanical fields such as on shear, oscillatory loading, extension etc., with account taken of kinetic phenomena. The simplest though far from realistic model of the polymer molecule in solution is a bead. A more complex model is an ellipsoid; even more complex is the dumbbell model [66-70].

The general task of kinetic theories based on mechanical models of polymer is a comparison of the actually observed behavior with predictions
following from the analysis of the behavior of a model and the estimation of the role of the constants introduced to characterize the elements of the models, which are supposed to correspond to certain molecular parameters of the real polymeric chain.

The first widely accepted model to understand the behavior of polymer solutions was of Rouse [71]. In the year 1953, Rouse proposed his bead spring model. This model is also known as Kargin-Slonimsky-Rouse model [66]. According to this model, each macromolecular chain is subdivided into several segments that are large enough to obey Gaussian statistics. Here all the segments are assumed to be identical and have identical Viscoelastic properties, but each of which is deformed independently of the others. The mass of the segment which is responsible for energy dissipated by the moving segment in a viscous medium is represented by bead. The connectivity of the chain is assumed to be provided by the connection of the beads through springs, which accounts for elastic nature of the macromolecule. Therefore a macromolecular chain is considered to be a succession of ‘n’ beads interconnected by (n-1) springs.

The Rouse model to some extent could successfully describe the Brownian motion of a polymer chain, but unfortunately its conclusions did not agree with experimental results. According to Rouse model, the diffusion constant (D) and the relaxation time (τ) depend on the polymer molecular weight M as follows:

\[ D \propto M^{-1} \]

\[ \tau \propto M^{2.28} \]

However, experimental observation yielded that,

\[ D \propto M^{-1} \]

\[ \tau \propto M^{3.29} \]

Here, the exponent \( \nu \) is a factor that used to express the dependence of the polymer size on molecular weight (in \( \theta \) solvent \( \nu=1/2 \) and in good solvents \( \nu=3/5 \)) [68].
The Rouse model is linear by nature; therefore it can well describe the systems that are within the framework of the linear theory of viscoelasticity. The reason for the discrepancy between experimental and Rouse model is due to the fact that, the average velocity of a particular bead is determined only by the external force acting on it, and is considered to be independent of motion of the other beads. However, in reality the motion of one bead is influenced by the motion of the surrounding beads through the medium of the solvent [66-68]. In spite of its draw backs, Rouse model played historically an important role in physics of polymers since it demonstrated the possibilities of the molecular statistical approach to the analysis of the relaxation properties of polymeric systems.

Owing to the drawbacks of Rouse theory which failed to reproduce the long time relaxation dynamics of the polymeric solution systems, Zimm [72] in the year 1956 proposed a model which is also known as Kirkwood-Riseman-Zimm (KRZ) model [66]. In his proposal Zimm modified the bead-spring model to include hydrodynamic interaction effects. The Zimm theory uses the assumptions of the Rouse theory and in addition considers hydrodynamic interactions between the moving segments and the solvent. The theory also makes use of the method formulated by Kirkwood and Riseman [66] for the evaluation of the viscosity of dilute polymer solutions.

In dilute solutions there exists a long range interaction between segments mediated by the flow of the solvent, which is called the hydrodynamic interaction. When a segment moves in a solvent, it draws the surrounding solvent, and induces local flow. Such a local flow propagates in the solvent and causes an induced flow field at a distant point, which imposes a force on the segment at the point. As result, long range force is produced between two segments.
Recently Wolf et al. [73,74] have given an elaborate discussion on the effect of hydrodynamic interaction in various polymer/solvent systems based on the above theories. Wolf et al. theory is based on the idea that energy dissipation at the interface is quantified by viscosity \( \eta \) of polymer solutions and should be governed by the surface fractions of the molecules rather than by their volume or weight fractions.

The key equation to the present approach is the interrelation between surface fractions \( \Omega \) and volume fractions \( \phi \) given by

\[
\Omega = \frac{(1 + \gamma)\phi}{(1 + \gamma \phi)}
\]

where \( \gamma \) measures the differences in the ratio of surfaces \( F \) and volume \( V \) of the components and is defined as

\[
\gamma = \frac{(F_2/V_2)}{(F_1/V_1)} - 1
\]

The molecular surfaces required in that context can be calculated, in a first approximation, from chemical formulas of the compounds by means of tabulated increments [75]. However, since these data are based on thermodynamic information and in view of the fact that the efficiency of some surface elements might differ for thermodynamic interaction, as compared with intermolecular friction, one should be cautious. An analogous problem does not exist with molecular volumes. For mixtures containing polymers that are too short to entangle, the required \( \gamma \) value can therefore at least be estimated, if not predicted.

In the following, the compositions of polymer solutions are given in terms of their volume fraction \( \phi \) or surface fraction \( \Omega \), where 1 stands for the solvent and 2 for the polymer; in some cases 2 is omitted for simplicity. In order to clear
out large difference in the viscosities of the components quantified by the parameter $\delta$ according to

$$\delta = \ln \eta_2 - \ln \eta_1$$

The discussion will be mainly conveyed in terms of excess viscosities (deviation from Arrhenius law) is defined as

$$\Delta \ln \eta = \ln \eta - (1 - \varphi) \ln \eta_1 - \varphi \ln \eta_2$$

Assuming that the dissipation of energy at the interfaces between like molecules and excluding specific interactions between the components, one can formulate an ideal mixing law for the viscosity $\eta$ of the mixture in terms of surface fractions $\Omega$ of its components as

$$\ln \eta = \Omega_1 \ln \eta_{11} + 2\Omega_1 \Omega_2 \ln \eta_{12} + \Omega_2 \ln \eta_{22}$$

$\eta_{11} = \eta_1$ and $\eta_{22} = \eta_2$ represent the friction between like molecules and $\eta_{12}$ measures the mutual friction between the different components.

In the absence of specific thermodynamic interactions, as in the case of mixtures of chain molecules made of identical monomeric units and differing in their length only, the following expression for $\eta_{12}$ turned out to describe such systems quantitatively:

$$\eta_{12} = \exp[\alpha + m(1 - \Omega)](\eta_{11}\eta_{22})^{0.5}$$

In which the hydrodynamic interaction parameter $\alpha$ measures the excess friction between the polymer and its solvent in the limit of vanishing solvent concentration ($\Omega \to 1$; free draining of coils). The parameter $m$ accounts for the
effects of collective motion; it increases the term in the square bracket of the above relation to $\alpha + m$ (the correction for non-ideal intermolecular friction) in the limit of infinitely dilute solution ($\Omega \rightarrow 0$; non-draining coils). For phenomenological considerations, it is clear that the parameter $m$ constitutes a composite quantity for which the following relations hold true:

$$m = \frac{[\eta] \rho}{2(1 + \gamma)} \frac{\delta - \alpha}{2}  \tag{2.35}$$

Where the product of intrinsic viscosity $[\eta]$ and polymer density $\rho$ represents the inverse of $\Phi^*$, the volume fraction of the total space filled by the polymer coils.

Substituting all the above equations in equation (2.32), one gets

$$\Delta \ln \eta = \left\{ \delta \left[ \gamma (1 + \gamma \rho)^2 - (1 - \varphi)(1 + \gamma) \right] + 2\alpha (1 + \gamma)^2 \varphi + [\eta] \rho (1 - \varphi) \right\} \frac{\varphi (1 - \varphi)}{(1 + \gamma \rho)^3} \tag{2.36}$$

For polymer/polymer mixtures, we have modified the relations of Wolf et.al theory [73,74] to evaluate the parameters of the theory using free volume data since viscosity and free volume are inversely related [30]. The final resulting equation from which the hydrodynamic interaction parameter $\alpha$ can be evaluated is

$$\Delta F_v = \left\{ \delta \left[ \gamma (1 + \gamma \varphi_2)^2 - \varphi_1 (1 + \gamma) \right] + 2\alpha (1 + \gamma)^2 \varphi_2 + e^{\frac{1}{\rho_1}} \rho \varphi \right\} \frac{(1 + \gamma \varphi_2)^3}{\rho_1 \rho_2} \tag{2.37}$$
the left hand side quantity $\Delta F_v$ in equation (2.37) is calculated as,

$$\Delta F_v = \left[ \frac{1}{F_v} - \frac{\phi_1}{F_{v1}} - \frac{\phi_2}{F_{v2}} \right]^{-1}$$  \hspace{1cm} 2.38

in which the right hand side parameters are known fully known from positron data. $\delta$ in equation (2.37) is defined as $\delta = \frac{1}{F_{v2}} - \frac{1}{F_{v1}}$, in terms of fractional free volumes which is the difference between the reciprocal of the fractional free volumes of the pure polymers. In the above equations $\rho$ is the density of the blend, $\phi_1$ and $\phi_2$ are volume fractions of the blend constituents. It has been observed that $\alpha$ attains large negative values in case of miscible systems indicative of good thermodynamic mixing and it decreases and approaches close zero with decrease in miscibility level.

The geometry factor $\gamma$ in equation (2.37) is evaluated from the following relation [76], since we know $\phi_1$, $\phi_2$, $F_v$, $F_{v1}$ and $F_{v2}$.

$$F_v = \left[ \frac{\phi_1}{F_{v1}} + \frac{\phi_2}{F_{v2}} + \delta \left( \frac{\gamma \phi_1 \phi_2}{1 + \gamma \phi_2} \right) \right]^{-1}$$  \hspace{1cm} 2.39

The $\gamma$ parameter is a measure of the surface fractions to quantify the geometrical effects in the molecular architecture particularly involving changes in conformation and the resulting close packing, which contains the effect of unequal size of molecules of identical shape as well as that resulting from differences in the molecular architecture. The $\alpha$ parameter is a measure of excess friction at the phase boundaries between the chains of constituent polymers. This accounts for the resultant deformation of the molecular chain segments in the system and particularly at the interface between the polymer components or in other words the parameter $\alpha$ is a measure of the adhesion strength at the
interface. In case of phase separated blends, chain entanglements do not generate additional friction in the system and in such a situation \( \alpha \) takes very small values. If the friction at the interface is high, this results in increased dissipation of energy which produces less tension at the interface thereby fine dispersion. This is indicated by large negative values of \( \alpha \). By monitoring the changes in this parameter the changes at the interface can be better understood compared to just free volume parameters.

### 2.5 Positron Method

#### 2.5.1 Thermalization of Positrons

The process in which, high-energy positrons lose energy by inelastic collisions with atoms and molecules of the medium and slow down to thermal energies (~kT) is called **Positron thermalization**. Before annihilation, positron thermalization in the medium is an important starting point because it justifies the assumption that the momenta of positrons are very small compared to the momenta of electrons with which they undergo annihilation. With decreasing energy, the interactions span various processes such as ionization, creation of electron-hole pairs and positron-phonon interactions. Electronic excitations can be in the form of electron-hole pair production or of collective plasmon excitations of valence electrons in the material [77]. The work of Mikeska [78] suggests that the positron-phonon interaction do play a significant role in the thermalization process. Bergersen and Pajanne [79], Puska and Nieminen [80] have reviewed the theoretical work on positron thermalization. Earlier, Garwin [81] and Lee-whiting [82] have done calculations, which showed that a positron would be expected to thermalize in a time shorter when compared to its annihilation time. Calculation of the time required for thermalization through the
excitation of electron-hole pairs by Carbotte and Arora [83] gave values somewhat larger than those deduced by Lee-whiting [82] and this discrepancy may be due to the arbitrary choice of positron-electron interactions made by the former group. In addition to this, Kubica and Stewart [84] have experimentally demonstrated that positrons in metals reach thermal or very near thermal velocities prior to annihilation even at sample temperatures as low as 4.2 K. In condensed matter, the positron thermalization depends on the electron density in the surroundings. All positrons irrespective of their initial energies reach thermal energies in a time of the order of $10^{-12}$ second or even less. Experimentally it has been well established that the total thermalization time $\tau_R = 10^{-12}$ second is shorter when compared to the lifetime of positron in matter $\tau \approx 10^{10}$ second [85]. During this thermalization process, the positron combines with an electron of the surrounding medium to form Positronium (Ps) atom. The Ps so born with a binding energy of 6.8 eV also thermalizes like positron and spends most of its lifetime at thermal energies [86].

After thermalization, the positron diffuses into the solid as a free Bloch wave in a perfect lattice, having a distribution, which is peaked, in the interstices between atomic cores [87,88]. Thereafter, positron lives in thermal equilibrium with the environment and its state develops in real space as diffusion process in which the positron interaction with phonons are quasi-electric i.e., positron momentum is conserved [80]. During diffusion, the positron interacts with defects in the solid and trapping of positron into a localized state may happen. The motion of thermalized positrons in solids is limited by positron-electron interaction described by electron-hole pair generation, positron lattice interaction and scattering by impurities. Thus, an understanding of the mobility and its
temperature dependence is also important for a proper interpretation of the trapping process at defects.

In case of metals, the positrons get localized or trapped at point defects such as vacancies and in molecular solids positrons can form an atomic bound state called Positronium, which can also become localized or trapped at defects such as voids (free volume) present in the condensed medium. Eventually the positron and Positronium annihilate resulting in the emission of gamma rays, which carry the information out of the material. The thermalization and positron diffusion process can be described as the evolution of the positron distribution function in the momentum and the real spaces. The distribution function can be obtained, in principle, by solving the Boltzmann equation [80].

Thus, all positrons irrespective of their initial (non relativistic) energies reach thermal energies in a time of the order of a pico second or even less [77] and during this thermalization process they form Ps. The formation of Ps in the molecular medium has been a matter of strong debate [85,89,90]. There are several models of positronium formation, which were reviewed in a monograph by Mogensen [91]. In the following section different models explaining positronium (Ps) formation are briefly discussed.

### 2.5.2 Positronium formation:

In chapter I, the formation of Positronium and its decay is introduced briefly. The mechanism of positronium formation in various material medium has been explained using various models namely, Ore gap model, Spur model, resonant model, blob model, bubble model etc. The first general theory was published by Ore in the year 1949. Of the above models, the Ore gap model has been used frequently by many researchers [92]. The spur model also finds equal
emphasis in the discussion of Ps formation and in recent times positron researchers seem to realize the significance and usefulness of this model in understanding Ps formation mechanism.

(i) Ore gap model

The energy range most favourable for positronium formation is called Ore gap after its Norwegian discoverer Aadne Ore [92]. The theory was originally proposed for gases but, with some restrictions, it was also tried for liquids as well as solids.

According to this model, Ps formation is probable when the positron energy during its slowing down process lies within a gap where there is no electronic energy transfer is possible. Ps formation can occur at energies \( E_{\text{ex}} - (E_i - 6.8) \) eV. \( E_i \) is the ionization potential of the medium, 6.8 eV is the binding energy of the Ps, and \( E_{\text{ex}} \) is an excitation level that exists in the range \( E_i - (E_i - 6.8) \) eV.

The higher energy limit for positronium formation is governed by the requirement that the kinetic energy of Ps cannot be higher than its binding energy, otherwise it will decompose in a very short time. Kinetic conditions lower this limit. Usually positron energy should not exceed the ionization potential of the gas because, in that case, ionization would be the more probable process than Ps formation. Even at this decreased energy level, Ps formation probability is small. It reaches considerable values only if the positron energy is lower than the lowest excitation energy of gas atoms. Above this limit, positrons are likely to excite the atoms of the substance than to form Ps. Thus the width of the Ore gap becomes:

\[
\Delta = E_{\text{ex}} - (E_i - 6.8) \text{ eV}
\]

2.40
The formation of Ps has been successfully explained by this model in gases [93-98] and it has been modified to explain the Ps formation in solids [38] and in liquids [99]. In a condensed phase, conditions determining Ps formation are much more complicated. Generally, even some crucial parameters such as ionization potential, solvating effect, etc are known with insufficient accuracy. Therefore for condensed matter a more probable model is the spur model. Though it does not give quantitative data and its equations change from material to material, its results are impressive.

(ii) Spur model

Mogensen [89] first proposed the spur model of Ps formation, but the quantitative formulation of this model was given by Tao [100]. The basic premise of this model is that when positron loses its last few 100 eV of kinetic energy, it creates a track, or the so called spur, in which it resides along with the atoms and molecules, ions and electrons. The electrostatic attraction between positron and electrons in the spur can result in Ps formation. The Ps formation will compete with other processes such as ion-electron recombination, diffusion of electrons out of the spur and annihilation of electrons with positron. This model indicates a correlation between the Ps formation probability and the properties of electron spurs studied in radiation chemistry [101,102].

It is based on the assumptions that:

(i) The positron and secondary electrons knocked out during the last several acts of ionizations thermalize within the same volume, and positive ions also reside there.

(ii) Secondary electrons recombine with the same probability either with the positive ions or with the positrons. Therefore the probability that the positron
gets an electron for subsequent Ps formation is \( n_0/(1+n_0) \), where \( n_0 \) is the initial number of ion-electron pair in the terminal spur.

A semi-quantitative picture of Ps formation in a spur of a dense gas was developed by Mogensen [103] and Jacobsen [104,105]. If the positron is at a distance \( r \) from an electron at the end of their thermalization, with the assumption that there is only one electron in the spur then the probability of positronium formation in the spur, in the absence of other competing processes, can be written in the Onsager [106] form as \( 1-e^{\frac{r}{r_c}} \) where ‘\( r_c \)’ is the critical or ongager radius for a medium of dielectric constant \( \varepsilon \) and is given by,

\[
r_c = \frac{\varepsilon^2}{4\pi \varepsilon kT}
\]

which is the separation at which the attractive Coulomb energy is \( kT \). Thus if the pair separation upon thermalization \( r \) is \( >> r_c \) positronium formation is uncertain. The positronium formation fraction in molecular gases is expected to depend on both density and temperature and has been given by Jacobsen [105] in an approach, which is a combination of Ore and spur models and is given by

\[
P_{Ps} = \frac{n_0}{1+n_0} \left( 1-e^{\frac{-r}{r_c}} \right) e^{(-\lambda_f \tau_{Ps})}
\]

The last exponential takes into account a possibility of the free positron annihilation occurring during Ps formation time, \( \tau_{Ps} \), with the annihilation rate \( \lambda_f \). Therefore, the contribution from this factor is negligible. In non-polar molecular media at room temperature \( r_c \) is \( \approx 300\text{Å} \). Typical thermalization length ‘\( r \)’ is \( \approx 100 \text{Å} \). Therefore, the Onsager factor \( 1-e^{\frac{r}{r_c}} \) is close to unity. By considering
the observable values of $P_s$ yields which is 0.7 and the above equation it can be estimated that the terminal positron spur contains 2 to 3 ion-electron pairs.

However, the spur model is inconsistent with the structure of the positron track. The interaction of the injecting positron with the matter could be considered similar to the behavior of energized electron. Two important facts that have to be taken into account at this stage are: (i) ionization energy of such a positron (electron) is about 1-4 eV/Å, which means that positron effectively ionizes molecules at the end of its track; (ii) motion of the $e^+$ in the blob is diffusion like. Therefore, based on the above facts, it could be realized that the terminal positron track is not a spur, containing 2 or 3 ion-electron pairs, but the blob, containing about 30 overlapped ion-electron pairs [107-110]. Particularly it implies that the multiparticle nature of the terminal part of the $e^+$ track cannot be correctly taken into account through the factor $n_o/(1+n_o)$.

(iii) **The blob model**

In depth understanding of the spur model exploited the fact that the terminal positron track consists blob of about 30 overlapped ion-electron pairs. Therefore another model, which was proposed to explain the mechanism of positronium formation, was blob model [111,112].

The important properties of blob model that is at the end part of positron track are:

(i) **Terminal blob consists of about 30 overlapped ion-electron pairs, with a blob radius $r_{bl}$ of about 40 Å.**

(ii) **Due to the strong Coulombic interaction, intra blob electrons adjust their motion to the distribution of primary positive ions and screen**
them. As a result the width of the spatial distribution of electrons is only slightly larger than that of ions.

(iii) Since there is attraction between electrons and ions, the expansion of blob is governed by ambipolar diffusion. As a result, out-diffusion of electrons is almost completely suppressed.

After the last ionization event in the terminal blob, the positron and intra blob electrons become sub ionizing and excite intra- and intermolecular vibrations. Due to the screening effect and fluctuation in the local electric field the electrons cannot transfer their kinetic energy to excitations of vibrations. This effect lengthens the thermalization of electrons and ion-electron recombination process. Therefore, this provides surplus electrons for the positron to undergo the formation of positronium.

If the positron is thermalized outside the blob, the only way for it to form Ps is to diffuse back in to the blob and pick one of the intra blob electrons. To pick up an electron the initial separation between $e^+$ and $e^-$ must be comparable to the average distance between intra blob species which is $\approx 20\text{Å}$.

(iv) Resonant model

Recently, Ito and Zhang [107] have proposed a new model for Ps formation called Resonant model. This model emphasizes the importance of excited molecular states as precursor to Ps formation. The Ps formation from these excited molecular states is a resonant electron transfer process and this view is extended to Ps formation from epithermal positrons. Actually, this model comprises of two stages. In the first stage, the epithermal positron and the ground state molecule forms the resonant excited state. The second stage is the Ps formation from nearly thermal positron and the excited molecule [107]. The
formation of resonant Ps must be formulated in two stages: epithermal and spur stages. Epithermal stage occurs during thermalization of positron and involves resonant Ps formation. Positron that failed to form Ps in the epithermal stage thermalizes in the spur and can form Ps. Thus, the resonant model of Ps formation contains aspects of both Ore model and the Spur model to some extent. This model needs further experimental verification before its use in a large way.

(v) The Free volume model

Another important model for Ps formation is the free volume model, which was proposed and developed by Brandt et al. [41]. This model was originally developed to deal with the decay of Ps which takes place in vacancies and other open spaces, the so-called free volume holes in polymers. It assumes that Ps is formed only in a free volume which is larger than a certain critical value. Although the energy at which the positron picks up an electron to form Ps cannot be explained by the free volume model, it does explain the sites where Ps may be formed in molecular solids. Unlike metals, molecular solids contain a large fraction of imperfect sites, such as impurities, defects, voids, grain boundaries, cavities etc. Many of these sites serve as sites for Ps formation. Furthermore, the average electron density of molecular solids is lower than that of metals, so the o-Ps lifetime is essentially distinguishable from that of the positron. Unlike alkali halides, where the lifetimes of quasi-Ps states (~0.4 ns) are only about twice those in positron states (0.2 to 0.3 ns), Ps in molecular substrates has a lifetime greater than 0.5 ns which can be unambiguously distinguished from that of positrons [41].
2.5.3 Positron states and Annihilation characteristics

The annihilation of positrons with electrons is accompanied by the emission of one, two, or more photons ($\gamma$-quanta). Single-photon positron-electron annihilation is possible only in the presence of a third body (a nucleus or electrons) that carries away the recoil momentum. When a free positron and a nearly free electron (atomic) annihilate, at least two photons are created. The positron annihilation cross section rapidly decreases with an increase in the number of emitted photons. As the number of created photons increases by one, the annihilation cross section is multiplied by the fine-structure constant $\alpha = 1/137$, i.e. the probability of the annihilation process decreases more than by two orders of magnitude. Dirac calculated the cross section of two-photon annihilation of a free positron and a free electron. In the non-relativistic approximation, this cross section increases with decreasing relative velocity $v$ of the colliding particles [80, 85]:

$$\sigma_D = \sigma_{2\gamma} = \pi r_0^2 \frac{c}{v}$$  \hspace{1cm} 2.43

where $r_0$ is the classical electron radius, and $c$ is the speed of light. As $v \to 0$, the cross section $\sigma_D$ becomes infinite. However, the positron annihilation rate $\lambda_D$ tends to a finite limit:

$$\lambda_D = \sigma_D v n_e = \pi r_0^2 c n_e$$  \hspace{1cm} 2.44

where $n_e$ is the electron density at the site of annihilation.

Positron-electron annihilation is possible only if the energy and momentum conservation laws are met, which in the case of two-photon annihilation have the form,

$$k_1 + k_2 = p = 2mv$$  \hspace{1cm} 2.45
Here $m = m_0 / \sqrt{1 - v^2 / c^2}$, where $m_0$ is the electron rest mass, $k_1$ and $k_2$ are the photon momenta, $E$ is the energy of positron-electron pair, $v$ is the relative velocity of center of mass of positron-electron pair in the laboratory frame of reference. The vector diagram of $k_1$ and $k_2$ is shown in Figure 2.4.

Equations (2.45) and (2.46) imply that if the pair's center of mass in the laboratory system of coordinates is fixed ($v=0$), the two photons fly apart in opposite directions (angle $\theta$ in Figure 2.1 goes to zero) with the same energy: $k_1c = k_2c = m_0c^2 = 0.511$ MeV. When $v \neq 0$, the angle between the directions in which the photons fly apart differs from $180^\circ$ and their energy is not equal to 0.511 MeV. If the pair momentum $p \ll m_0c^2$, the deviation angle $\theta$ (See Figure 2.4) is defined by

$$\sin \theta \approx \frac{p_\perp}{m_0c}$$

And the change in photon energy (the Doppler shift) is given by the formula

$$\Delta E_\gamma \approx \frac{p_\parallel c}{2}$$

Thus, in case of two-photon annihilation, measuring the deviation angle $\theta$ of the photons from $180^\circ$ or the Doppler shift $\Delta E_\gamma$ of the annihilation line ($0.511$
MeV) makes it possible, at least in principle, to determine the momentum of positron-electron pair in the laboratory frame of reference. In the case of three-photon annihilation, the conservation laws do not unambiguously determine the momenta and energies of the emerging photons. At $v = 0$, all the photons fly apart in the same plane. The deviation angle (for $v \neq 0$) from this plane is of the order $v/c$. In contrast to two-photon annihilation, the photons that are created in three-photon annihilation have a continuous energy from 0 to 0.511 MeV.

The various positron states yield specific annihilation characteristics, which can be experimentally observed in the positron lifetime and Doppler broadening experiments. The positron wave function $\Psi_+(\vec{r})$ can be calculated from one-particle Schrödinger equation [80,85]:

$$-rac{\hbar^2}{2m} \nabla^2 \Psi_+(\vec{r}) + V(\vec{r})\Psi_+(\vec{r}) = E_+ \Psi_+(\vec{r}) \quad 2.49$$

where the positron potential consists of two parts:

$$V(\vec{r}) = V_{\text{Coul}}(\vec{r}) + V_{\text{con}}(\vec{r}) \quad 2.50$$

The first term is the electrostatic Coulomb potential and the second term takes into account the electron-positron correlation effects in the local density approximation. Many practical schemes exist for solving the positron state $\Psi_+(\vec{r})$ from the Schrödinger equation [80,85].

A positron state can be experimentally characterized by measuring the positron lifetime and momentum distribution of the annihilation radiation. These quantities can be easily calculated once the corresponding electronic structure is known. The positron annihilation rate $\lambda$, the inverse of lifetime $\tau$, is proportional to the overlap of the electron and positron densities:

$$\frac{1}{\tau} = \lambda = \pi r_e^2 c \int d\vec{r} |\psi_+(\vec{r})|^2 n_e(\vec{r}) \gamma[n_e(\vec{r})] \quad 2.51$$
where \( r_e \) is the classical radius of the electron, \( c \) the velocity of light, \( n_e(\bar{r}) \) the electron density, and \( \gamma[n_e] \) the enhancement factor of the electron density at the positron site [87].

References


22. LA Utracki, “*Polymer Alloys and Blends*”, Hanser Verlag, 1990, NY.


